

Theoretical Electronic Structure Studies of Ideal Diamond/Metal Interfaces*

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We have begun computational studies of the electronic properties of several ideal epitaxial interfaces of diamond with Ni and Cu, both of which are closely lattice matched. We are particularly interested in shedding light on the mechanism responsible for formation of the Schottky barrier, not yet fully understood at the microscopic level. Our calculations are of the standard self-consistent local-density-approximation variety; most were carried out with a new Gaussian-based local-orbital method of Erwin, Pederson and Pickett[1], and some with the linear-augmented-plane-wave (LAPW) method of Krakauer and coworkers[2].

The interfaces are modelled as supercells, with slabs sufficiently thick to ensure that the diamond bandgap is well-formed in the layers farthest from the interface. Since diamond has only been successfully doped p-type, we calculate barrier heights Φ_B for hole conduction, $\Phi_B = E_F - E_{VBM}$, where E_F is the Fermi level and E_{VBM} is the diamond valence band (VB) maximum, determined from the density of states (DOS) projected onto the layer farthest from the interface. Further details may be found in an earlier study of the diamond/Ni (001) interface[3], and in an expanded version of the present report[4].

For the diamond/Ni (111) interface, we have investigated two different orientations of the diamond and Ni surfaces: (i) the "on top" orientation, in which Ni atoms are placed directly atop surface C atoms, so as to maintain tetrahedral coordination of the surface C atoms, and (ii) the T_4 position, in which Ni atoms sit directly atop subsurface C atoms, i.e., in a 3-fold hollow formed by surface C atoms. The two choices reflect our intuitive notions of the relevant bonding considerations for C and Ni, respectively. The "on top" position is the most likely position for satisfying the single C dangling bond at this surface, while the T_4 position is a site of high coordination, presumably favorable for metallic bonding at the Ni surface.

The results for our two choices of orientation are strikingly different. In Figs. 1(a) and 1(b) we show the layer-projected local DOS (LDOS) for the "on top" and T_4 orientations, respectively. For the "on top" orientation, the C-layers are characterized by a nearly vanishing LDOS in the optical gap region, except at the interface layer, where a large feature with sharply defined structure appears. We have previously found that a similar feature occurs for the analogous orientation of the (001) interface, and have shown that its origin is almost entirely C dangling-bond states[3]. The gap states for this orientation are entirely localized at the interface layer, as is evident from the very small contribution to the DOS from layers away from the interface. At the central C layer, the LDOS is described reasonably well by the bulk diamond DOS, shown as a dotted curve in the topmost panels of Fig. 1. The Fermi level and VB maximum for this orientation are nearly coincident, so that Φ_B for this orientation is approximately zero. An otherwise identical calculation with the C-Ni layer separation reduced by 10% showed very similar results, including a zero height Schottky barrier.

For the T_4 orientation the situation is quite different. At the interface C layer of Fig. 1 (b), most of the gap region is filled in by a broad, relatively featureless LDOS, typical of the MIGS that are found in other Schottky barrier calculations[5]. Further evidence of MIGS formation is found in the C layers away from the interface, for which substantial contributions to the gap LDOS persist all the way in to the central layer. This is in marked contrast to the vanishing LDOS in these layers for the "on top" orientation. As expected, the density from these gap states consists of bulk Ni contributions joined onto a combination of C p-states that decays as it penetrates into the diamond slab. The decay is approximately exponential, with an estimated decay length in the range 2-3 Å, similar to the values found for a variety of narrow-gap, covalent semiconductors[6]. The LDOS for the central C layer can again be reasonably well matched to the bulk diamond DOS, giving the T_4 barrier height as $\Phi_B = 1.7$ eV. Examination of the valence charge density shows that the surface Ni atoms are indeed taking advantage of the high coordination on the diamond side. Evidently, bonding occurs between the Ni surface and both the surface and 1st subsurface layers of C atoms. All of these results are summarized in Table I.

Although we have not yet carried out total energy studies for these interfaces, experimental results for $\text{CaF}_2/\text{Si}(111)$ [7], as well as calculations for a Li monolayer on Si (111)[8], indicate that the minimum total energy orientation for this interface is the T_4 site. Assuming such findings (which we are presently pursuing) to hold for the present systems, we may tentatively conclude from our results

that (i) formation of the Schottky barrier is strongly dependent on the interface geometry, and may be contingent on a geometry near the total energy minimum; (ii) although bond formation and Φ_B are related, the presence of sp^3 -like bonds does not guarantee a non-zero value for Φ_B . Apparently, it is more important for the surface geometry to provide for high coordination of the surface metal atoms. Once there is sufficient overlap between metal and semiconductor states, MIGS can form, in this case with decay lengths characteristic of narrow gap semiconductors. On the basis of previous arguments[6], the Fermi level will then be pinned at a position independent of both the metal and the remaining details of the interface geometry. We emphasize, however, that this conclusion is warranted only if one assumes an interface orientation at or near the total energy minimum.

All reported experimental values for diamond/metal Schottky barrier heights involve the (111) interface, although none is available for Ni or Cu. For diamond/Au, reported values are in the range 1.3–2.0 eV; for diamond/Al, the range is 1.5–2.2 eV, and for diamond/Ba a single result of 2.0 eV has been published (references for all experimental data are found in Ref. 3). Our result of 1.7 eV for diamond/Ni (111) thus appears quite reasonable. All of these results fall around 1/3 of the bandgap (relative to the VB maximum), also consistent with results for narrow-gap semiconductors[6].

For the less studied (001) interface, we have investigated the two orientations analogous to those chosen for the (111) interface. Corresponding to the "on top" position for the (111) is the position, 2-fold coordinated with respect to the C surface, known as the "bridge site." As before, it is presumed to promote tetrahedral bonding of C atoms at the interface layer. Likewise, in analogy to the T_4 site on the (111) surface, we have studied the 4-fold hollow at the center of each C surface layer square, which offers the highest coordination to the surface metal atoms.

For the diamond/Ni (001) interface in the bridge site orientation, the situation is similar to the "on top" orientation of the (111) interface. As we have described in detail in Ref. 3, there is little or no bonding across the interface. The occupied valence states at the interface C layer are predominantly p_z -like, with unoccupied dangling-bond p_x and p_y states lying in the gap region. The tetrahedral charge distribution is severely disrupted at the interface, bearing little resemblance to the bonds in the bulk. A sharp feature in the surface C layer LDOS appears at about midgap, with very small contributions from layers away from the interface. As we found for the analogous orientation in the (111) interface, the barrier height is essentially zero. We have also performed identical calculations with this orientation for the diamond/Cu (001) interface at both the bulk diamond and bulk Cu lattice constants (different by ~1%). The results were qualitatively the same in all regards, and a zero value for Φ_B was again obtained.

For the 4-fold orientation, the results are qualitatively similar to the T_4 orientation of the (111) interface. The calculated Schottky barrier is $\Phi_B=2.1$ eV, 25% larger than for the (111). The character of the MIGS is also similar, although the decay length is slightly smaller, suggesting somewhat weaker pinning of the Fermi level. Some weak bonding can be observed between the interface C and Ni atoms; the distribution of bonding charge is fairly delocalized, not surprising in view of the over-coordination of C atoms at the interface layer. All of these results are included in Table I.

It is clear, on the basis of both experimental and theoretical results, that a complete model of Schottky barrier formation must account for the dependence of Φ_B on interface orientation. The picture we propose, on the basis of the present diamond/metal calculations, holds that (i) an interface geometry near the total energy minimum, (ii) high coordination of the surface metal atoms, and (iii) formation of a potential barrier, are closely interrelated. Furthermore, bond formation is apparently closely tied to barrier formation, but does not guarantee it. Finally, on the basis of available experimental data and our findings for Φ_B and the MIGS decay length, we tentatively conclude that diamond Schottky barrier heights are not strongly dependent on the metal species, and that the description of moderate Fermi-level pinning by MIGS (at $\Phi_B=1.7$ and 2.1 eV for the (111) and (001) interfaces, respectively) is essentially correct.

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Table I. Summary of results for the various diamond/metal ideal interface calculations described in the text.

IF	Metal	Orientation	Bonding	Φ_B	Gap states
(111)	Ni	on top	weak sp^3	-0 eV	dangling bond
(111)	Ni	on top (10% red.)	weak sp^3	-0	dangling bond
(111)	Ni	T_4	5-fold	1.7	MIGS
(001)	Ni	bridge	weak	-0	dangling bond
(001)	Cu	bridge	weak	-0	dangling bond
(001)	Ni	4-fold hollow	delocalized	2.1	MIGS

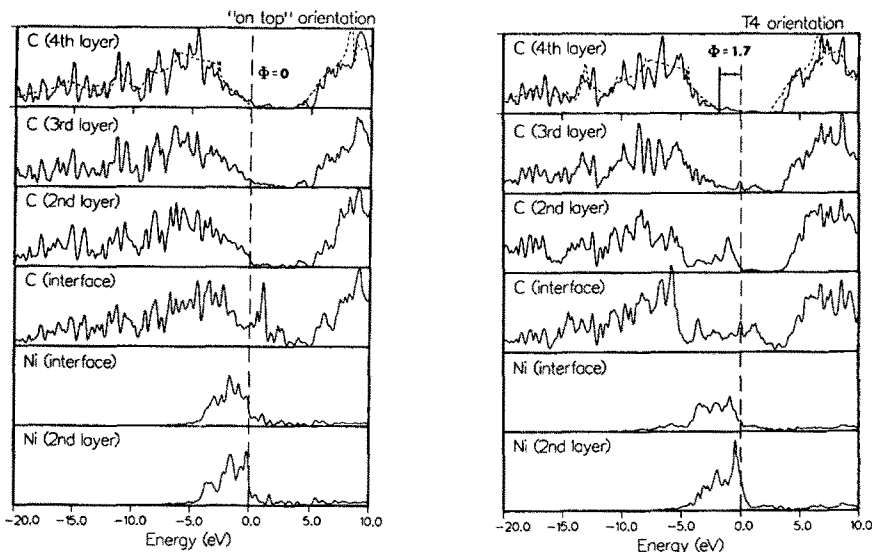


Fig. 1. Layer-projected local DOS for two diamond/Ni (111) interfaces. (a) For the "on top" orientation, the Schottky barrier is essentially zero, and the localized feature in the gap region of the interface C layer is primarily from C dangling bond states. (b) The T_4 orientation allows exponentially decaying metal-induced gap states (MIGS) to form in the diamond optical gap region, pinning the Fermi level and giving a Schottky barrier of 1.7 eV. The Ni and C LDOS panels differ by a factor of 10.